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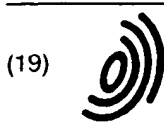
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**(54) ULTRAHIGH-MOLECULAR-WEIGHT POLYETHYLENE MOLDING FOR ARTIFICIAL JOINT AND PROCESS FOR PRODUCING THE MOLDING**

(57) The present invention relates to a ultra high molecular weight polyethylene molded article for artificial joints having molecular orientation of crystal orientation and to a method for preparing the same, wherein the polyethylene molded article having a low friction and excellent abrasion resistance is obtained by irradiating a low dose of a radioactive ray to the ultra high molecular weight polyethylene to introduce a small amount of crosslinking points within molecular chains, giving compression-deformation after melting at a high temperature around the melting point thereof, and cooling and solidifying.

**EP 0 729 981 A1**

## Description

## TECHNICAL FIELD

5 The present invention relates to an ultra high molecular weight polyethylene molded article suitable for artificial joints having molecular orientation or crystal orientation and to a method of preparing the same.

## BACKGROUND ART

10 It has been passed thirty years or more since an artificial joint was developed and applied clinically to patients suffering from any diseases of arthritis. Since then, benefits given by the artificial joint have been great in the sense of social welfare because, for example, patients with chronic rheumatism have come to be able to walk again and to return to public life. On the other hand, however, there have been occurred serious problems, particularly late complication caused by total joint arthroplasty, a high rate of occurrence of "loosening" in the implant components, necessity of revision with surgical operation caused by osteolysis around the implanted artificial joint.

15 The artificial joint includes artificial hip joint, artificial knee joint, artificial elbow joint, artificial finger joint, artificial shoulder joint and the like. Among those joints, it is necessary for the artificial hip joint and artificial knee joint to have high mechanical strength because gravity corresponding to several times of the patient's body weight is applied to them. Therefore, materials for the artificial joint at present are constituted of a hard material of metal or ceramic and a soft socket of an ultra high molecular weight polyethylene (UHMWPE). While the UHMWPE constituting such a socket is superior in abrasion resistance as compared with polymeric materials such as polytetrafluoroethylene and polycarbonate, the UHMWPE is inferior in properties such as low abrasion resistance and stress relaxation to impact load which are inherently possessed by articular cartilage of living body. Also, reaction caused by a foreign matter has been a serious problem wherein macrophages proliferate against wear debris of the UHMWPE socket, i.e. component and  
25 an abnormal granulation tissue generated thereby causes resorption of the bone.

After artificial joints have been developed, though some improvements in qualities of material and design have been made, for example, a cementless artificial joint and the like with respect to the hard material, there has been no remarkable progress for about thirty years with respect to the soft socket portion except that the UHMWPE was employed. And if the artificial joint is used for a long period of time, numerous wear debris of polyethylene are produced  
30 because of friction between the hard material such as metal and the UHMWPE of the socket. By considering the osteolysis due to granulation tissue containing a foreign matter which is caused by the wear debris, further improvement of abrasion resistance is indispensable. As an attempt to reduce the abrasion of UHMWPE, it can be considered to select a material for the hard material and to improve the UHMWPE. Though the irradiation of an ultra high dose of  $\gamma$ -ray was tried for improving the UHMWPE, it was made clear that coefficient of abrasion increases and abrasion loss does not decrease. Also, though the improvement to increase molecular weight of the UHMWPE was made and a weight-average molecular weight of the UHMWPE at present has been increased to approximately 5 to 8 million, it is difficult to make a UHMWPE having a far ultra high molecular weight. Further, considerable improvement in dynamic properties can scarcely be expected even if one having a weight-average molecular weight of 10 million could be synthesized. Thus, it is regarded that any improvement in dynamic properties of the UHMWPE by chemical modification reaches its  
40 limitation, and it is regarded to be difficult to obtain a UHMWPE molded article having a more excellent abrasion resistance and lower friction.

It is well-known that Carothers of E.I. Du Pont developed, first all over the world, a synthetic fiber, i.e. Nylon and greatly contributed industrially. As means for improving mechanical properties of this synthetic fiber, uniaxial stretching in the direction of fiber axis is carried out industrially. Also, to improve strength of film, biaxial stretching and rolling are carried out industrially. In accordance with these methods, mechanical properties can be increased considerably by giving uniaxial orientation or biaxial orientation to molecules or crystals.

From these points of view, there is an idea that orientation is given to molecules or crystals in the polymer structure to improve the mechanical properties. However, any technologies cannot endow molecules or crystals with orientation in a large molded article in the form of block, and it is not easy to consider an enable method.

50 Then, the present inventors tried to obtain a molded article of a low friction and to improve an abrasion resistance by introducing molecular orientation or crystal orientation into a finished product by means of not a chemical modification method but a physical modification method.

This approach has never been attempted not only in Japan but also in other countries. The idea to endow the polyethylene molded article for artificial joints with molecular orientation or crystal orientation is the very creative, and it is  
55 sure that this invention, if actually carried out, is applied to the artificial joints of all over the world. Also, this invention will be revolutionary industrial innovation whereby disadvantages which have been problem for the past thirty years are improved.

DISCLOSURE OF THE INVENTION

The invention relates to an ultra high molecular weight polyethylene (UHMWPE) molded article for artificial joints and to an artificial joint comprising the UHMWPE molded article.

5 This UHMWPE molded article having molecular orientation or crystal orientation can be obtained by irradiating a low dose of a high energy ray to a raw UHMWPE molded article to introduce a very small amount of crosslinking points in polymer chains to be crosslinked slightly, then by compression-deforming the crosslinked UHMWPE molded article after heating up to its compression-deformable temperature, and by cooling the molded article with keeping the deformed state.

10 The UHMWPE molded article having molecular orientation or crystal orientation (hereinafter referred to as "oriented UHMWPE molded article") of the present invention has a low friction and remarkably improved abrasion resistance. And, the artificial joint comprising the oriented UHMWPE molded article has a smooth lubricity and reduced amount of abrasion loss.

15 BEST MODE FOR CARRYING OUT INVENTION

The oriented UHMWPE molded article of the invention has the molecular orientation or crystal orientation within the molded article. The meaning of "to have molecular orientation within the molded article" is that polymer chains are oriented perpendicular to the direction of the compression, namely, oriented to the direction of the flow of molecular chains. The meaning of "to have crystal orientation" is that the crystal planes in polyethylene such as (200) plane and (110) plane are oriented to the direction parallel to the compression plane, namely, that the crystal planes are oriented. Also, the presence of these orientations can be known by means of birefringence measurements, infrared spectra and X-ray diffraction. And, a coefficient of friction of the molded article decreases and an abrasion loss also decreases by endowing with those orientations. Also, other functional properties, for example, tensile strength and tensile modulus are improved, and also density, thermal properties (melting point, heat of fusion) and the like are improved.

As described above, the oriented UHMWPE molded article can be obtained by irradiating a high energy ray to the raw UHMWPE and then heating up and compression-deforming the UHMWPE, followed by cooling and solidifying.

As the raw UHMWPE, one having a weight-average molecular weight of 2 to 8 million, preferably 5 to 7 million is used. The melting point thereof is approximately 136° to 139°C. The raw UHMWPE is used usually in the form of block, and may be used in the form of rod.

Every kind of high energy rays can be employed as the high energy ray to be irradiated, for example a radioactive ray such as  $\gamma$ -ray or X-ray, an electron beam, a neutron ray and the like. Among them,  $\gamma$ -ray is superior in views of availability of irradiation apparatus and excellent permeability to materials. This irradiation of the high energy ray is carried out to generate crosslinking points in the molecular chains of the UHMWPE and then to produce intermolecular crosslinkage. The density of crosslinking is preferably such a very small degree that the crystallization is not prevented with ensuring a large elastic-deformation, for example 0.1 to 10, particularly 1 to 2 crosslinking points per one molecular chain.

With respect to the irradiation atmosphere, if oxygen exists, it is not preferable since a decomposition (cleavage) occurs simultaneously, and therefore the atmosphere in vacuum or of an inert gas such as  $N_2$  or argon is preferable. The temperature of the atmosphere may be room temperature and also may be a higher temperature of not less than the crystal transition point (80°C).

The dose of irradiation (energy) is very important. If the dose of irradiation is too high, the density of crosslinking becomes higher, and the bridged structure is destroyed if a large deformation is applied in the subsequent process. And, even if the molten state is made, such a degree of elastic deformation required to obtain the desired molecular orientation or crystal orientation cannot be given. As a result, it is obliged to decrease a degree of the deformation, and it becomes impossible to obtain the molecular orientation or crystal orientation which is necessary for molecular chains in the molded article. On the other hand, in case that a dose of irradiation is too low or no irradiation is carried out, molecular chains are fluidized in the manner of viscous fluidity without stretching to be plastic-deformed, resulting in that the molecular orientation or crystal orientation cannot be obtained. A preferable dose of irradiation (energy) is the dose to give the above-mentioned density of crosslinking and 0.01 to 5.0 MR, preferably 0.1 to 3 MR in case of radioactive rays.

The UHMWPE molded article which is crosslinked slightly by irradiating the high energy ray has an infinite weight-average molecular weight because it is crosslinked, and the melting point thereof changes not so much and is 136° to 139°C.

55 Then, this slightly crosslinked UHMWPE molded article is heated up to a compression-deformable temperature. The compression-deformable temperature of is a temperature of around or not less than the melting point of the crosslinked UHMWPE, and is concretely from the melting point minus 50°C to the melting point plus 80°C. It is most suitable to heat up to a temperature of not less than the melting point, particularly preferably 160° to 220°C, further preferably 180° to 200°C to melt completely. The compression-deformation can be carried out, however, at a temperature

of even around the melting point, for example 100° to 130°C. If completely melted, since the crosslinked UHMWPE is in the state of rubber to possess rubber elasticity, the compression-deformation is easily carried out.

The compression-deformation is carried out under a pressure of 30 to 200 kgf/cm<sup>2</sup>, usually 50 to 100 kgf/cm<sup>2</sup> with heating at the above-mentioned temperature in a die suitable for the use or by using a hot press machine. It is sufficient that a degree of the compression is approximately 1/3 to 1/10 of an original thickness in case of a molded article in the form of block. The deformation of the crosslinked UHMWPE molded article of the present invention is a rubber elastic deformation because molecular chains are crosslinked slightly, and after the molecular chains are stretched to give the necessary molecular orientation, then cooled as they are and crystallized, the crystal orientation can be obtained. On the other hand, non-crosslinked, namely non-irradiated UHMWPE molded article is fluid-deformed when heated and compressed at a temperature of not less than the melting point, and thus molecular orientation or crystal orientation cannot be obtained.

Then, the UHMWPE molded article having the molecular orientation or crystal orientation obtained by the compression-deformation as described above is cooled and solidified with keeping the deformed state. If the deformed state is set free before solidified, the stretched molecular chains are relaxed in stress to return to the original state because the compression-deformation is conducted in the molten state. That is, the molecular orientation or crystal orientation in the UHMWPE molded article is relaxed in a moment. Therefore, the deformed state must not be set free until solidified.

As the cooling method, there are rapid coolings such as water-cooling and air-cooling as well as standing to cool, and the cooling is carried out down to room temperature, preferably to a temperature of around 20° to 40°C. Further, it is preferable to cool at a constant rate under a condition of 10°C/min, preferably 1°C/min to obtain excellent dynamic properties because the cooling rate has a great influence on the crystallinity, particularly on the degree of crystallinity of the produced molded article. The completion of the solidification can be confirmed by decrease of a pressure gauge (the volume being shrunk after the completion of the crystallization).

Also, before the cooling the compression-deformed UHMWPE molded article may be subjected to isothermal crystallization at around 100° to 130°C, preferably 110° to 120°C for 1 to 20 hours, preferably 5 to 10 hours with keeping the deformed state, and then cooled to room temperature, preferably to 40°C and solidified. When carrying out the isothermal crystallization, the degree of crystallinity becomes higher and the dynamic properties are improved. The cooling after the isothermal crystallization is not particularly limited and the cooling at a rate of 1°C/min is preferable.

The melting point of the UHMWPE molded article having the molecular orientation or crystal orientation obtained by the cooling and solidification is 135° to 155°C.

The compression-deformed molded article which is obtained as described above can also be processed to a socket for artificial joints by cutting and can be molded by means of the compression-deformation mold with a die comprising a convex and concave portions. The surface hardness can be further reinforced by introducing metal ions, e.g. titanium, zirconium, iron, molybdenum, aluminium and/or cobalt ion into the UHMWPE molded article for artificial joints which is obtained by cutting the compression-deformed molded article.

Hereinafter, the present invention is explained concretely by referring to Preparation Examples and Examples.

#### PREPARATION EXAMPLES 1 TO 3

A block of UHMWPE (thickness 3 cm, width 5 cm, length 5 cm) having a weight-average molecular weight of approximately 6 million and a melting point: 138°C was put in a glass ampul and the glass was sealed after reducing the inner pressure ( $10^{-2}$  to  $10^{-3}$  mmHg) under vacuum.  $\gamma$ -Ray from cobalt 60 was irradiated at a dose of 0.5 MR to this glass ampul at 25°C. Then, the UHMWPE block irradiated by the radioactive ray (melting point: 138°C, weight-average molecular weight: infinite) was taken out from the glass ampul, melted completely at 200°C by using a hot press, compressed to 1/3, 1/4.5 and 1/6 of the original thickness by applying a pressure of 50 kgf/cm<sup>2</sup>, and then cooled to room temperature through natural cooling with keeping the deformed state.

#### COMPARATIVE PREPARATION EXAMPLES 1 TO 3

The same raw UHMWPE block as was used in Preparation Examples 1 to 3 was compressed to 1/3, 1/4.5 and 1/6 of the original thickness after melting completely at 200°C by using a hot press in the same way without irradiation, and cooled naturally to room temperature with keeping the deformed state.

#### PREPARATION EXAMPLES 4 TO 6

Irradiated UHMWPE molded articles were obtained by compression-deforming and cooling naturally similarly in Preparation Example 1 except that a dose of irradiation of  $\gamma$ -ray was changed to 1.0 MR, 1.5 MR or 2.0 MR. Each weight-average molecular weights of 1.0 MR irradiated article, 1.5 MR irradiated article and 2.0 MR irradiated article were infinite, and the melting points thereof were almost constant and were 138°C.

## PREPARATION EXAMPLE 7

An irradiated UHMWPE molded article was obtained similarly in Preparation Example 1 except that after the irradiation of  $\gamma$ -ray (0.5 MR), the temperature was raised to 130°C and the compression-deformation to 1/3 was carried out under a pressure of 200 kgf/cm<sup>3</sup> for 5 minutes.

## PREPARATION EXAMPLE 8

An irradiated UHMWPE molded article was obtained similarly in Preparation Example 1 except that after the compression molding, the isothermal crystallization was carried out for 10 hours at 120°C and then the natural cooling was carried out.

## EXAMPLE 1

The test sample having a thickness of 7 mm and a diameter of 7 mm was prepared by cutting from the UHMWPE molded article obtained in each of Preparation Examples 1 to 8 and Comparative Preparation Examples 1 to 3, and a wear factor and coefficient of friction were evaluated by measuring a friction force and wear factor as the followings.

Testing apparatus and testing conditions:

The unidirectional Pin-On-Disc wear and friction testing machine manufactured by Research Center for Biomedical Engineering, Kyoto University was used for the test.

The unidirectional-type testing machine is operated by pressing a test sample on a surface of a ceramic disc, which is rotating in the clockwise direction, by means of the arm-type loading method. The load can be varied by providing a weight to the one end of the arm. The rotation of the disc is transmitted to a bearing by way of a belt according to the rotation of an inverter-controlled motor. The testing speed was set to 50 mm/s. Also, all tests were carried out in 50 ml saline for 48 hours and the temperature of the liquid was kept at  $25 \pm 2^\circ\text{C}$ .

Means to measure frictional force and wear volume:

A friction force was measured by a lever type dynamometer fixed to the arm portion of the testing machine. The friction force was recorded with a pen recorder with the lapse of time. The friction coefficients shown in test results (Table 1) were determined in case of a sliding distance of 8640 m (48 hours after tests begin).

The wear volume was evaluated by compressing the rotating disc of zirconia at a pressure of 1 MPa and by measuring the decreased thickness of the test sample with a non-contact type capacitance level gauge.

The test for each test sample was carried out three times under each loading condition, and the coefficient of friction and coefficient of abrasion were calculated in average value. In this case, the surface of the zirconia disc was made in intentionally roughened to Ra: 0.2 to 0.3, and the wear volume was measured after 48 hours.

Wear factor and coefficient of friction were calculated according to the equation of Dowson et al.

$$\text{Wear Factor (WF)} = \text{Wear volume (mm}^3\text{)} / (\text{Load (N)} \times \text{Sliding distance (m)})$$

$$\text{Coefficient of friction (CF)} = \text{Friction force (N)} / \text{Load (N)}$$

The test results are shown in Table 1. With respect to the non-irradiated sample, there is no substantial difference in the wear factor (WF), that is, WF of  $15.3 \times 10^{-7}$  for the sample having the compression ratio at deformation (original thickness/thickness after compression-deformation) of 3, WF of  $16.4 \times 10^{-7}$  for the compression ratio of 4.5, and WF of  $14.9 \times 10^{-7}$  for the compression ratio of 6.

Remarkable decrease was observed, however, with respect to the 0.5 MR irradiated sample, i.e. WF of  $9.07 \times 10^{-7}$  for the compression ratio of 3, WF of  $2.78 \times 10^{-7}$  for the compression ratio of 4.5, and WF of  $5.31 \times 10^{-8}$  for the compression ratio is 6.

## EXAMPLE 2

Characteristics of the UHMWPE molded articles obtained in Preparation Example 3 and Comparative Preparation Example 3 are shown in Table 2.

The heat of fusion and melting point were measured at a scan speed of 10°C/min by means of DSC-50 of SHIMADZU CORPORATION. And, the tensile strength and Young's modulus were measured at a tensile rate of 100%/min by means of Autograph S-100 of SHIMADZU CORPORATION.

As shown in Table 2, the density and melting point of UHMWPE molded article obtained from the 0.5 MR irradiation test of Preparation Example 3 are higher and the tensile strength and Young's modulus thereof increases, as compared with those of the UHMWPE molded article obtained from the non-irradiation test of Comparative Preparation Example 3. Particularly, the melting point rises from 138.0° to 149.5°C.

TABLE 1

Preparation Example	Dose of irradiation MR	Compression deformation		Cooling	Wear factor (WF)	Coefficient of friction (CF)
		Temperature (°C)	ratio			
1	0.5	200	3	standing to cool	$9.07 \times 10^{-7}$	0.11
2	0.5	200	4.5	standing to cool	$2.78 \times 10^{-7}$	0.08
3	0.5	200	6	standing to cool	$5.31 \times 10^{-8}$	0.03
4	1.0	200	3	standing to cool	$7.35 \times 10^{-7}$	0.04
5	1.5	200	3	standing to cool	$4.62 \times 10^{-7}$	0.02
6	2.0	200	3	standing to cool	$8.31 \times 10^{-8}$	0.01
7	1.0	130	3	standing to cool	$9.64 \times 10^{-7}$	0.12
8	1.0	200	3	allowed to cool after the isothermal crystallization for 10 hours at 120°C	$2.53 \times 10^{-8}$	0.01
Comparative Preparation Example						
1	-	200	3	standing to cool	$15.3 \times 10^{-7}$	0.14
2	-	200	4.5	standing to cool	$16.4 \times 10^{-7}$	0.15
3	-	200	6	standing to cool	$14.9 \times 10^{-7}$	0.12

TABLE 2

Sample	Density (g/cm <sup>3</sup> )	Heat of fusion (cal/g)	Melting point (°C)	Tensile strength (kg/cm <sup>2</sup> )	Young's modulus (kg/cm <sup>2</sup> )
Comparative Preparation Example 3	0.931	31.6	138.0	$0.3 \times 10^3$	$1.36 \times 10^4$
Preparation Example 3	0.948	39.2	149.5	$1.3 \times 10^3$	$1.95 \times 10^4$



## INDUSTRIAL APPLICABILITY

The ultra high molecular weight polyethylene molded article for artificial joints obtained according to the present invention has the molecular orientation or crystal orientation in the molded article, and is low in friction and is superior in abrasion resistance, and therefore is available as a components of artificial joints.

Further, the ultra high molecular weight polyethylene molded article for artificial joints of the present invention can be used as a component for artificial hip joints (artificial acetabular cup), a component for artificial knee joints (artificial tibial insert) and the socket for artificial elbow joints, and in addition to the medical use, it can be applied as materials for various industries by utilizing the characteristics such as low friction and superior abrasion resistance.

## Claims

1. Ultra high molecular weight polyethylene molded articles having molecular orientation or crystal orientation.
2. The molded articles of Claim 1, wherein the ultra high molecular weight polyethylene having molecular orientation or crystal orientation is crosslinked slightly.
3. The molded articles of Claim 1 or 2, wherein a melting point of the ultra high molecular weight polyethylene molded article is 135° to 155°C.
4. Artificial joints comprising the molded article of any one of Claims 1 to 3.
5. A method for producing an ultra high molecular weight polyethylene molded article having molecular orientation or crystal orientation, wherein the ultra high molecular weight polyethylene molded article is crosslinked slightly by irradiating a high energy ray and introducing a very small amount of crosslinking points into molecular chains, and the crosslinked ultra high molecular weight polyethylene molded article is compression-deformed after heating up to a compression deformable temperature and then cooled with keeping the deformed state.
6. The method of Claim 5, wherein the high energy ray is a radioactive ray and a dose of the irradiation is 0.01 to 5.0 MR.
7. The method of Claim 5 or 6, wherein the compression-deformable temperature is a temperature in the range of a melting point of the crosslinked ultra high molecular weight polyethylene minus 50°C to the melting point plus 80°C.
8. The method of Claim 5, 6 or 7 wherein a weight-average molecular weight of the ultra high molecular weight polyethylene before irradiation is 2 to 8 million.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01858

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>6</sup> C08F110/02, C08F2/54, A61L27/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup> C08F110/00-110/14, C08F2/00-2/60, A61L27/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 62-243634, A (Nippon Oil Co., Ltd.), October 24, 1987 (24. 10. 87), Claim, line 13, upper right column to line 3, lower right column, page 6 & JP, 6-39499, B2	1-3, 4-8
Y	Edit by Polymer Society "Polymer Functional Material Series (Vol. 9) Medical Treatment Functional Material", November 20, 1990 (20. 11. 90), Kyoritsu Shuppan K.K. P. 165-166	4
Y	Edit by Polymer Society "Polymer New Material One Point (Vol. 20) Medical Polymer Material" February 20, 1989 (20. 02. 89), Kyoritsu Shuppan K.K., P. 45-46	4
A	JP, 4-198201, A (Komatsu Ltd.), July 17, 1992 (17. 07. 92), Claim (Family: none)	1-3, 5-8

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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